Stereochemical structures of some polyacrylates studied by one-dimensional and two-dimensional ^{13}C–^1H n.m.r. spectroscopy

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The stereochemical structures of samples of poly(ethyl acrylate) (PEA), poly(butyl acrylate) (PBuA) and poly(2-ethylhexyl acrylate) (PEHA), prepared by group transfer and anionic polymerization, were studied by ^{13}C and ^1H n.m.r. spectroscopy. The main-chain CH_2 spectral range was analysed by the application of the inverse ^{13}C–^1H HETCOR two-dimensional n.m.r. technique. A very similar HETCOR pattern was found for all polymers studied. In all cases, main-chain CH_2 lines in the ^1H and ^{13}C n.m.r. spectra could be assigned to configurational tetrads; for PEA and PBuA a partial assignment of carbon resonances to configurational hexads was possible. While PEHA prepared both by group transfer and anionic polymerization and PEA prepared by group transfer polymerization can be well approximated by Bernoullian statistics, for PEA and PBuA prepared by anionic polymerixation a first-order Markov model is required to fit the observed intensities at the hexad level.

(Keywords: stereochemical structures; polyacrylates; two-dimensional n.m.r.)

INTRODUCTION

N.m.r. spectroscopy is probably the most efficient technique for characterizing the stereochemical structure of polymers, because the chemical shift is sensitive to the configurational structure in sequences of monomeric units[1,2]. By using higher magnetic fields, resolved lines from longer configurational sequences can be observed in the spectrum. For configurational analysis the lines in the n.m.r. spectrum have to be assigned to various stereochemical sequences in the polymer. Of the acrylate polymers, the configurational structure has been studied in poly(methyl acrylate) (PMA), poly(ethyl acrylate) (PEA), poly(isopropyl acrylate) (PiPA), poly(butyl acrylate) (PBuA) and poly(naphthyl acrylate) by classical one-dimensional ^{13}C n.m.r. spectroscopy[3–6]. Matsuzaki et al.[3] observed in the 25 MHz ^{13}C n.m.r. spectra of PMA and PiPA an indication of resolution into three components corresponding to various triads (CH) and groups of two or three tetrads (CH_2). Three CH_2 components assigned to groups of various tetrads were also observed in the 20 MHz ^{13}C n.m.r. spectrum of PBuA[4]. In a very recent paper, Goñi et al.[6] studied the configurational structure of PMA, PEA and PBuA by 75 MHz ^{13}C n.m.r. spectroscopy; they reported assignments of lines to various triads (CH), tetrads and even hexads (main-chain CH_2). While for PBuA their assignments were consistent with those given by Pham et al.[4], for PMA their tetrad assignment of the CH_2 region differs from that of Matsuzaki et al.[3].

In all the papers cited above that deal with polyacrylates, the assignment of the n.m.r. lines of CH_2 carbons to various tetrads (or even longer configurational sequences) was based on a comparison of the experimental intensities with those calculated assuming Bernoullian statistics from diad or triad data. Recently, we studied the stereochemical structure of poly(t-butyl acrylate) (PtBuA) by a combination of one-dimensional and two-dimensional n.m.r. methods[7]. For the CH_2 range we were able to assign lines in the ^1H and ^{13}C n.m.r. spectra of PtBuA solutions to configurational tetrads. For this purpose we found as essential the application of the inverse HETCOR (heteronuclear correlation) two-dimensional ^{13}C–^1H n.m.r. method, which enabled us to define the resonances of CH_2 carbons with equivalent and nonequivalent protons. In the work described in this paper, a similar approach was applied to samples of PEA, PBuA and poly(2-ethylhexyl acrylate) (PEHA) prepared by group transfer and anionic polymerization. The stereochemical structure of PEHA had not been studied before now.

EXPERIMENTAL

Samples

Two samples each of PEA and PEHA were prepared under different conditions. PEA I was prepared by group transfer polymerization in tetrahydrofuran (THF) at $-30°C$. The polymerization time was 76 min. 1-Methoxy-1-trimethylsilyloxy-2-methylpropene (MTS) was used as the initiator with tetrabutylammonium fluoride monohydrate (TBAF) as the catalyst. The number-average

molecular weight $\bar{M}_n$ determined by gel permeation chromatography (g.p.c.) was $33\,000\,\mathrm{g\,mol^{-1}}$. PEA II ($\bar{M}_n$(g.p.c.)$= 14\,800\,\mathrm{g\,mol^{-1}}$) was prepared by anionic polymerization in a mixture of toluene and THF (volume ratio 19:1) at -70°C. The polymerization time was 160 min, and t-butyl 2-lithioisobutyrate with lithium t-butoxide (molar ratio 1:9) was used as the initiator. PEHA I ($\bar{M}_n = 11\,400\,\mathrm{g\,mol^{-1}}$) was prepared by group transfer polymerization with MTS and TBAF in THF at -30°C. The polymerization time was 90 min. PEHA II ($\bar{M}_n \approx 20\,000\,\mathrm{g\,mol^{-1}}$) was prepared by anionic polymerization in a mixture of toluene and THF (volume ratio 9:1) at -60°C, initiated by t-butyl 2-lithioisobutyrate and lithium t-butoxide (molar ratio 1:3)[8,9]. A sample of PBuA ($\bar{M}_n \approx 11\,000\,\mathrm{g\,mol^{-1}}$) prepared by anionic polymerization in a mixture of toluene and THF was also studied. By analogy with the preparations of poly(methyl methacrylate) and PtBuA[7], it was assumed that samples prepared by group transfer polymerization (PEA I, PEHA I) would be atactic, while samples prepared by anionic polymerization (PEA II, PBuA, PEHA II) would be predominantly isotactic.
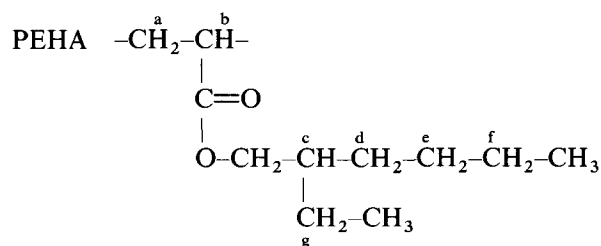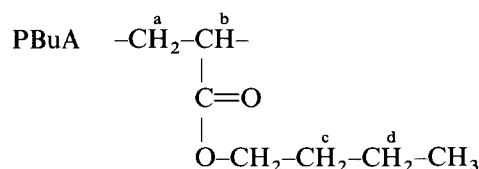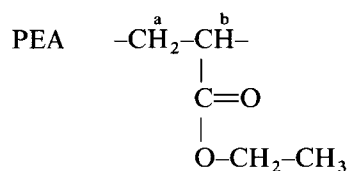
N.m.r. measurements

The 10% (w/v) solutions of PEA, PBuA and PEHA in C_6D_6 or $CDCl_3$ were studied in 5 mm tubes. Hexamethyldisiloxane (HMDS), with a signal at 0.05–0.1 ppm (depending on the solvent) from tetramethylsilane (TMS) in the ^{1}H n.m.r. spectra and at 2.0 ppm in the ^{13}C n.m.r. spectra, was used as the internal standard. All chemical shifts cited are referred to HMDS. N.m.r. spectra were measured at 70°C (C_6D_6) or 60°C ($CDCl_3$) using a Varian Unity 500 spectrometer operating at 499.8 MHz for ^{1}H n.m.r. and 125.7 MHz for ^{13}C n.m.r. Pulses at 30° with pulse intervals of 5.3 s and 5.9 s were used in the one-dimensional ^{13}C and ^{1}H n.m.r. measurements, respectively; these conditions enabled us to measure the correct intensities for all lines of the main-chain carbons and protons.

HMQC (heteronuclear multiple-quantum correlation; inverse HETCOR) spectra[10,11], which enabled us to achieve a much higher sensitivity compared to classical HETCOR, were obtained for all polymers in 10% solutions in C_6D_6 at 70°C. An HMQC spectrum of PEA in $CDCl_3$ at room temperature was also measured. In order to enhance the effectiveness of suppressing the signals of protons bound to ^{12}C, the BIRD[12] sequence was inserted before the beginning of the basic sequence. The delay separating the BIRD sequence from the basic HMQC sequence was set at 0.3 s. A total of 48 scans was accumulated over 420–512 t_1 increments with a relaxation delay of 0.5 s. A sine-bell apodization function with phase shift was applied in both dimensions prior to Fourier transformation. The total acquisition time was 12–13 h for every experiment.

RESULTS AND DISCUSSION

The major parts of the ^{1}H n.m.r. spectra for 10% solutions of the studied polymers in C_6D_6, measured at 70°C, are shown in *Figure 1*. For all polymers the resonances of the OCH_2 protons at ~ 4 ppm are not shown in this figure, nor are the resonances of the CH_3 protons at ~ 0.8–1.0 ppm. The assignments of proton resonances for PBuA and PEHA shown in *Figure 1* agree with those in the literature[4,9]. From the two-dimensional HETCOR spectra (see later on), it follows that for certain

tetrads in PEHA the resonances of the side-chain methine and main-chain methylene protons overlap in the peak at 1.6 ppm (*Figures 1d* and *1e*). Similarly, for PBuA (*Figure 1c*) the main-chain CH_2 resonances partly overlap the strong peak from the side-chain CH_2 protons at 1.5 ppm. The following structures show the assignments of the protons to the peaks in *Figure 1*.

PEA
$$-\overset{a}{C}H_2-\overset{b}{C}H-$$
$$|$$
$$C=O$$
$$|$$
$$O-CH_2-CH_3$$

PBuA
$$-\overset{a}{C}H_2-\overset{b}{C}H-$$
$$|$$
$$C=O$$
$$|$$
$$O-CH_2-\overset{c}{C}H_2-\overset{d}{C}H_2-CH_3$$

PEHA
$$-\overset{a}{C}H_2-\overset{b}{C}H-$$
$$|$$
$$C=O$$
$$|$$
$$O-CH_2-\overset{c}{C}H-\overset{d}{C}H_2-\overset{e}{C}H_2-\overset{f}{C}H_2-CH_3$$
$$|$$
$$\underset{g}{CH_2-CH_3}$$

In *Figure 2* are shown the ^{13}C n.m.r. spectra (the main-chain CH and CH_2 carbons only) for 10% solutions of all samples in C_6D_6, again measured at 70°C. For all the polymers studied, the CH_2 carbons are the most sensitive to the configurational structure. From *Figures 1* and *2* it is seen that in both the ^{1}H and ^{13}C n.m.r. spectra, the main-chain CH and CH_2 resonances are shifted to lower field in the sequence PEA, PBuA and PEHA, i.e. as the size of the side-chain substituent increases. While in the ^{13}C n.m.r. spectrum of PEA a fine band splitting occurs, reflecting the various populations of stereoisomeric sequences (pentads and hexads for main-chain CH and CH_2 carbons, respectively), for PEHA the line resolution for main-chain CH and CH_2 carbons is achieved only at the triad and tetrad levels even in the 125 MHz ^{13}C n.m.r. spectrum. On the other hand, the carbonyl carbons resonating at ~ 172.5 ppm (not shown in *Figure 2*) are also sensitive to the stereosequence (triads and pentads) for PBuA and PEHA, while for PEA this sensitivity is much lower (the whole range of chemical shifts for the carbonyl carbons being less than 0.2 ppm).

On the basis of a comparison of the main-chain methine resonances in the ^{13}C n.m.r. spectra of samples prepared by group transfer and anionic polymerization (assuming that polymers prepared by group transfer polymerization will be atactic, whereas polymers prepared by anionic polymerization will be isotactic), and in accordance with the assignments of methine resonances in the ^{13}C n.m.r. spectra of polyacrylates reported in the literature[3,5–7], we can state that in the methine range mm triads (or mm-centred sequences) appear at highest field. In our study of PtBuA[7] we found that methine bands of various triads are much better separated
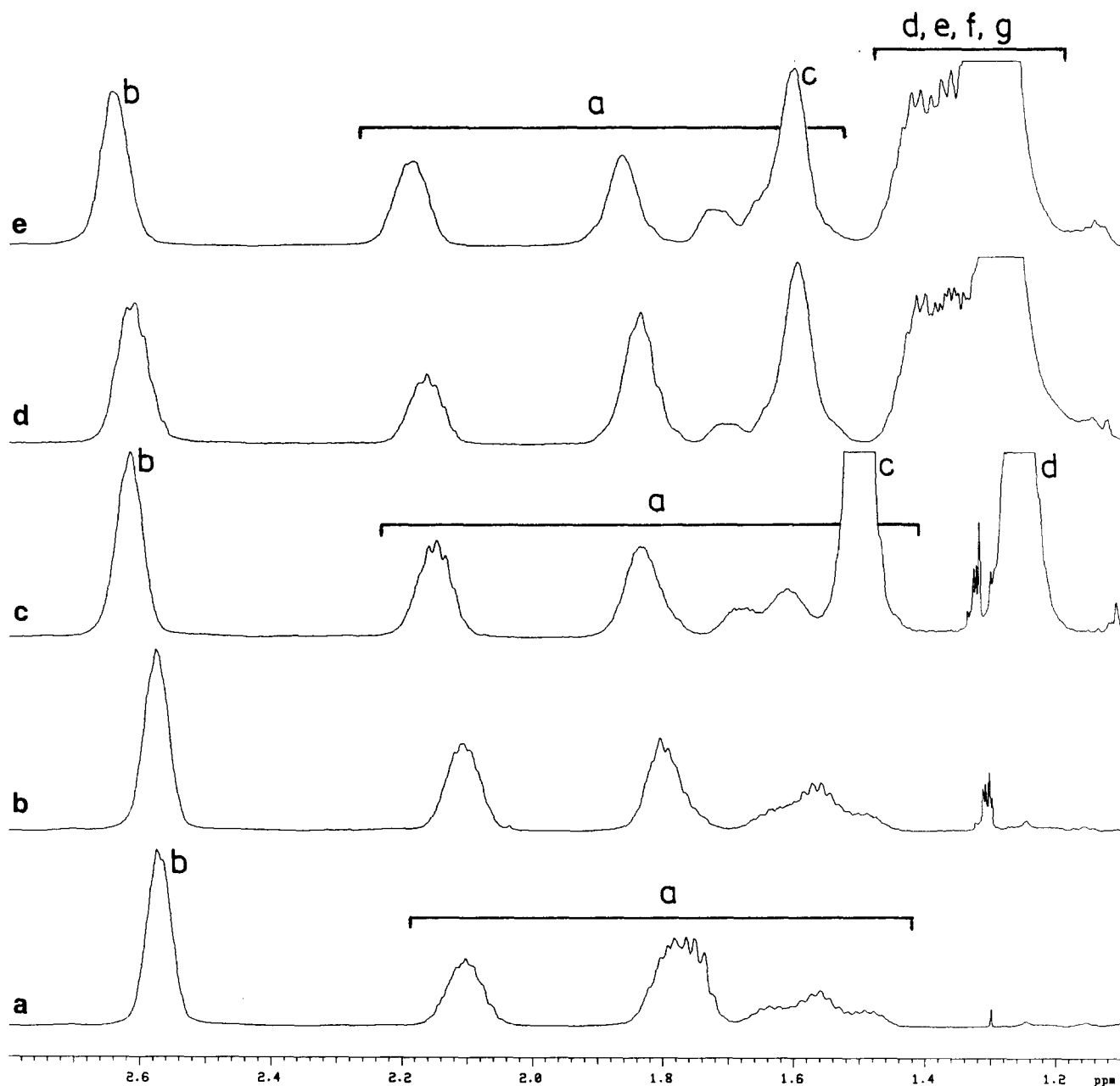
Figure 1 Parts of the 500 MHz ^1H n.m.r. spectra of C_6D_6 solutions (10% w/v) of (a) PEA I, (b) PEA II, (c) PBuA, (d) PEHA I and (e) PEHA II measured at 70°C

in the ^{13}C n.m.r. spectra of $CDCl_3$ solutions compared to C_6D_6 solutions. The methine resonances in the ^{13}C n.m.r. spectra of the polyacrylates studied in $CDCl_3$ are shown in *Figure 3*. While the bands of rr and mr triads still overlap, the band of mm triads is mostly well separated. By integration of the methine bands in the ^{13}C n.m.r. spectra of $CDCl_3$ solutions of the polyacrylates, the following populations of mm triads were obtained (with some uncertainty for PEHA I): PEA I (mm) = 0.30; PEA II (mm) = 0.36; PBuA (mm) = 0.38; PEHA I (mm) = 0.24; and PEHA II (mm) = 0.42.

The two-dimensional HETCOR ($^{13}C-^1H$) n.m.r. spectra for 10% solutions of PEA, PBuA and PEHA in C_6D_6, obtained by the inverse HETCOR (HMQC) technique, are shown in *Figures 4–6*. From *Figures 4–6* it follows that while in both the ^1H and ^{13}C n.m.r. domains the chemical shifts are somewhat different, the shapes of the HETCOR spectra are very similar for the various

polyacrylates, and also similar to the HETCOR spectra of PtBuA published in our previous paper[7]. The HETCOR spectrum of PEA I in $CDCl_3$ at room temperature was very similar to that shown in *Figure 4a*. Based on the similarity to the HETCOR spectra of PtBuA we have assigned particular resonances in the HETCOR spectra of PEA, PBuA and PEHA, as shown in *Figures 4–6*. These assignments were based on the fact that of the six n.m.r. resolvable tetrad sequences (mmm, mmr, mrm, mrr, rmr and rrr), three tetrads contain magnetically non-equivalent CH_2 protons (mmm, rmr and one of the mmr and mrr) and three contain magnetically equivalent CH_2 protons (rrr, mrm and one of the mmr and mrr). The assignments were also based on a comparison of the intensities of various resonances for samples prepared by group transfer polymerization (atactic) and anionic polymerization (isotactic). For PtBuA the correctness of the assignments of mmr and mrr resonances was also
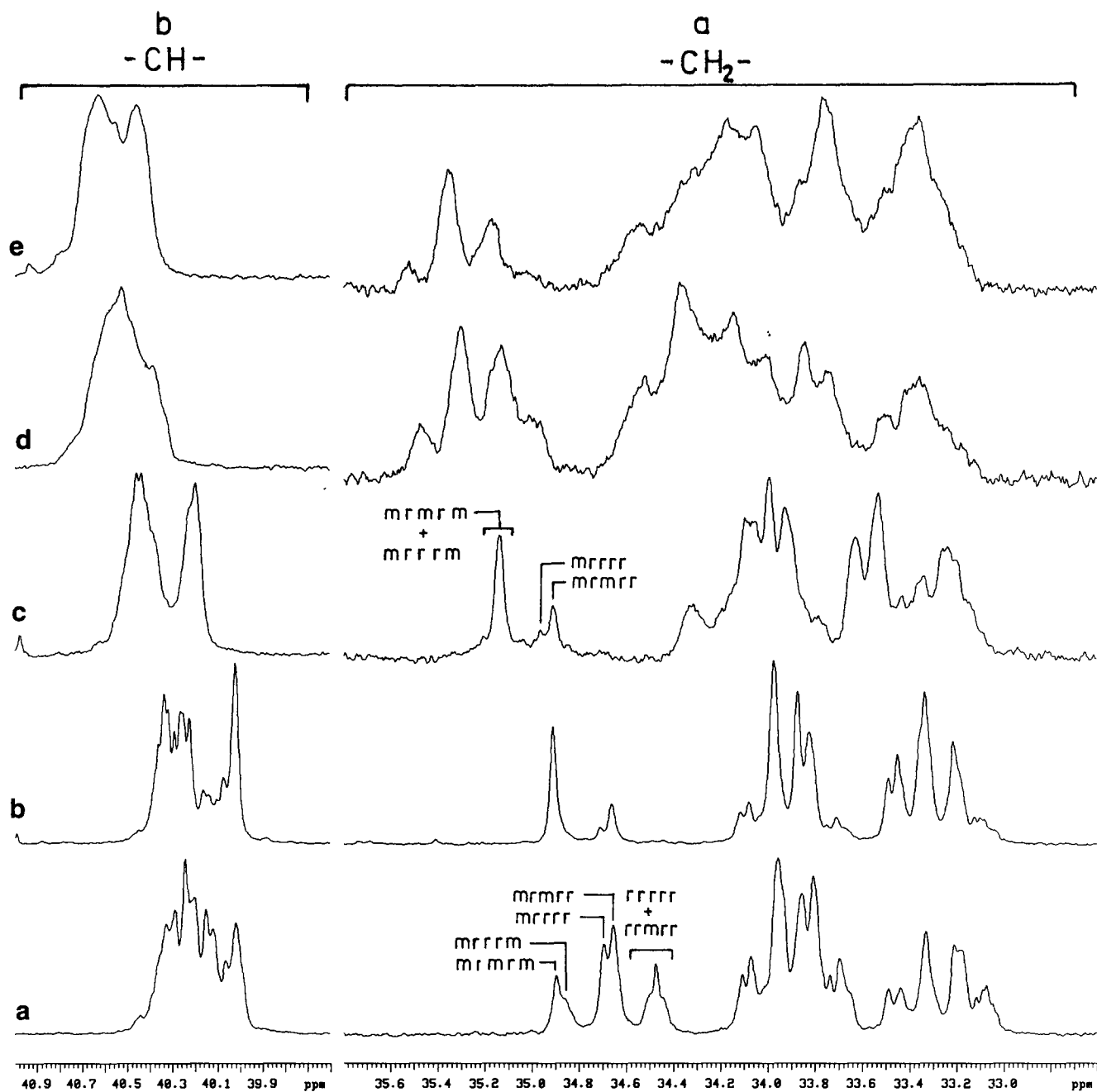
Figure 2 Regions of the main-chain methine and methylene resonances in the 125 MHz ^{13}C n.m.r. spectra of C_6D_6 solutions (10% w/v) of (a) PEA I, (b) PEA II, (c) PBuA, (d) PEHA I and (e) PEHA II measured at 70°C. The band intensities in the methine and methylene regions are not directly comparable

**Table 1** ^{13}C and ^{1}H n.m.r. chemical shifts of the methylene resonances for various tetrads of some polyacrylates in C_6D_6 (at 70°C)

Tetrad	^{13}C (ppm from HMDS)			^{1}H (ppm from HMDS)		
	PEA	PBuA	PEHA	PEA	PBuA	PEHA
mmm	33.0–33.5	33.1–33.6	33.2–33.7	1.62, 2.12	1.68, 2.16	1.71, 2.18
mrm	33.1–33.7	33.4–33.9	33.5–34.1	1.80	1.85	1.86
mmr	33.6–34.2	33.8–34.4	33.9–34.5	1.56, 2.11	1.62, 2.16	1.65, 2.18
mrr	33.8–34.3	34.0–34.6	34.2–34.7	1.78	1.84	1.86
rrr	34.3–35.0	35.3	35.0–35.6	1.75	1.80	1.84
rmr	34.5–35.1	34.9–35.4	35.1–35.5	1.48, 2.10	1.53, 2.16	1.56, 2.18

confirmed in the two-dimensional heteronuclear spin-lock relay spectrum[7]. The ^{13}C and ^{1}H n.m.r. chemical shifts for various tetrads in PEA, PBuA and PEHA are summarized in *Table 1*.

The HETCOR spectra presented in *Figures 4* and *5* prove that at the tetrad level, the assignments of the main-chain CH_2 carbon resonances as published recently for PEA and PBuA by Goñi *et al.*[6] and for PBuA by

Pham *et al.*[4] are wrong. For example, these authors assigned the band of CH_2 resonances at lowest field to rrr tetrads only. In such a case we should observe in the $^{13}C-^1H$ HETCOR spectrum only one peak for the respective carbons, because rrr tetrads necessarily have
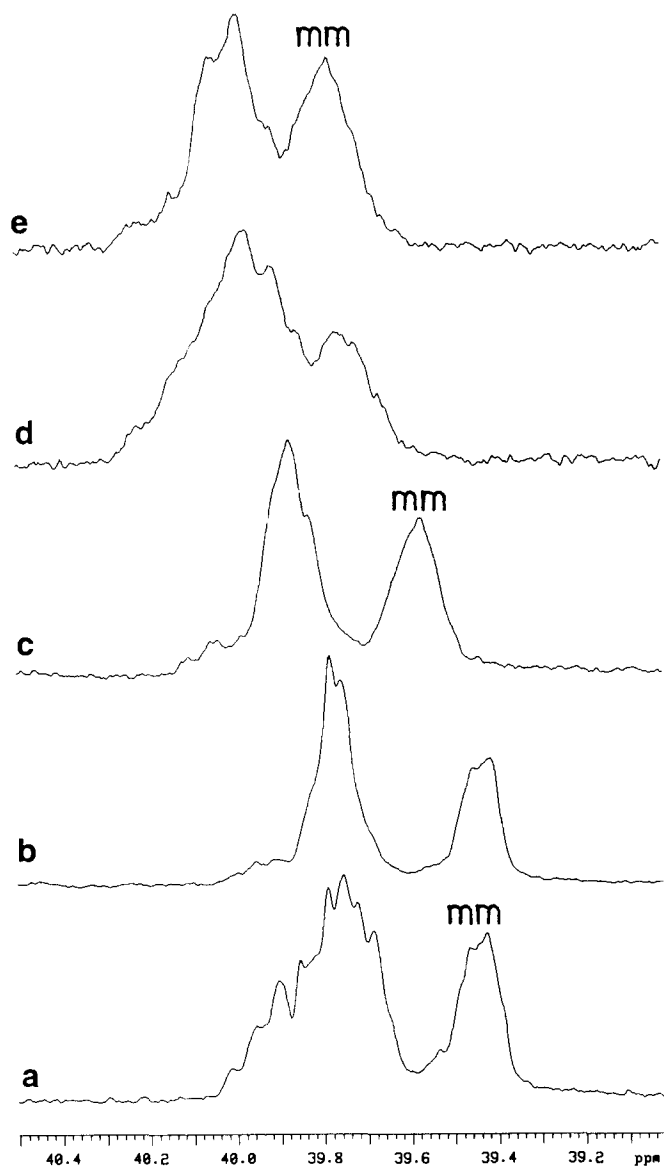
Figure 3 Regions of the main-chain methine resonances in the 125 MHz ^{13}C n.m.r. spectra of $CDCl_3$ solutions (10% w/v) of (a) PEA I, (b) PEA II, (c) PBuA, (d) PEHA I and (e) PEHA II measured at 60°C

equivalent protons. The existence of the three peaks in our HETCOR spectra proves that in the ^{13}C n.m.r. CH_2 band at lowest field, rrr resonances overlap the resonances of tetrads containing magnetically non-equivalent protons – rmr in this case. We assume that PMA (which we did not study) should also present a similar two-dimensional HETCOR pattern to those observed by us for PEA and PBuA. It should be noted that in this case our assignment is in agreement with the results obtained by Matsuzaki *et al.*[3], who assigned the three CH_2 components in the 25 MHz ^{13}C n.m.r. spectrum of PMA to the tetrad pairs rrr + rmr, mmr + mrr and mmm + mrm.

From the tetrad assignments shown in *Figures 4 6* it is evident that the main-chain CH_2 peaks appearing in the ^1H n.m.r. spectra at lowest field (2.1–2.2 ppm) represent protons downfield from all m-centred tetrads (rmr, mmr and mmm). The sum of the populations of all m-centred tetrads is equal to P_m, the population of the m diads in the polymer chain. By comparison of the integrated intensities of the downfield proton bands of m-centred tetrads at 2.1–2.2 ppm with the integrated intensity of the main-chain CH band (at ~2.6 ppm) we could easily obtain P_m values for all the polymers studied, and with these calculate the tetrad populations assuming Bernoullian statistics; the results are summarized in *Tables 2–4*. With the exception of PEA II, the values obtained in this way agree reasonably well with those based on P_m values obtained from the triad analysis of the main-chain CH regions in the ^{13}C n.m.r. spectra, as mentioned before, where again $P_m = (mm)^{1/2}$ assuming Bernoullian statistics. However, while for PEHA II the P_m value determined in this way is exactly the same as P_m from the ^1H n.m.r. spectrum, confirming the Bernoullian model for this polymer, for the other polymers the P_m values are somewhat different, indicating possible deviations from random statistics. From the values for m diads and mm triads determined from the ^1H n.m.r. spectra and from the analysis of the CH regions in the ^{13}C n.m.r. spectra, respectively, we could obtain the complete triad data; subsequently we could calculate the probabilities $P_{r/m}$ and $P_{m/r}$ and the populations of the various tetrads assuming first-order Markov statistics (see the Appendix). The calculated tetrad populations were compared with the experimental values, and for this purpose we divided the whole CH_2 region in ^{13}C n.m.r. spectrum (*Figure 2*) into three well separated regions (the integration limits are given for all the polymers in *Tables 2–4*). For PEA and PBuA (*Tables 2* and *3*) there is excellent agreement between the expected and found values for the tetrad

Table 2 Experimental and calculated tetrad contents for PEA obeying Bernoullian or first-order Markov statistics

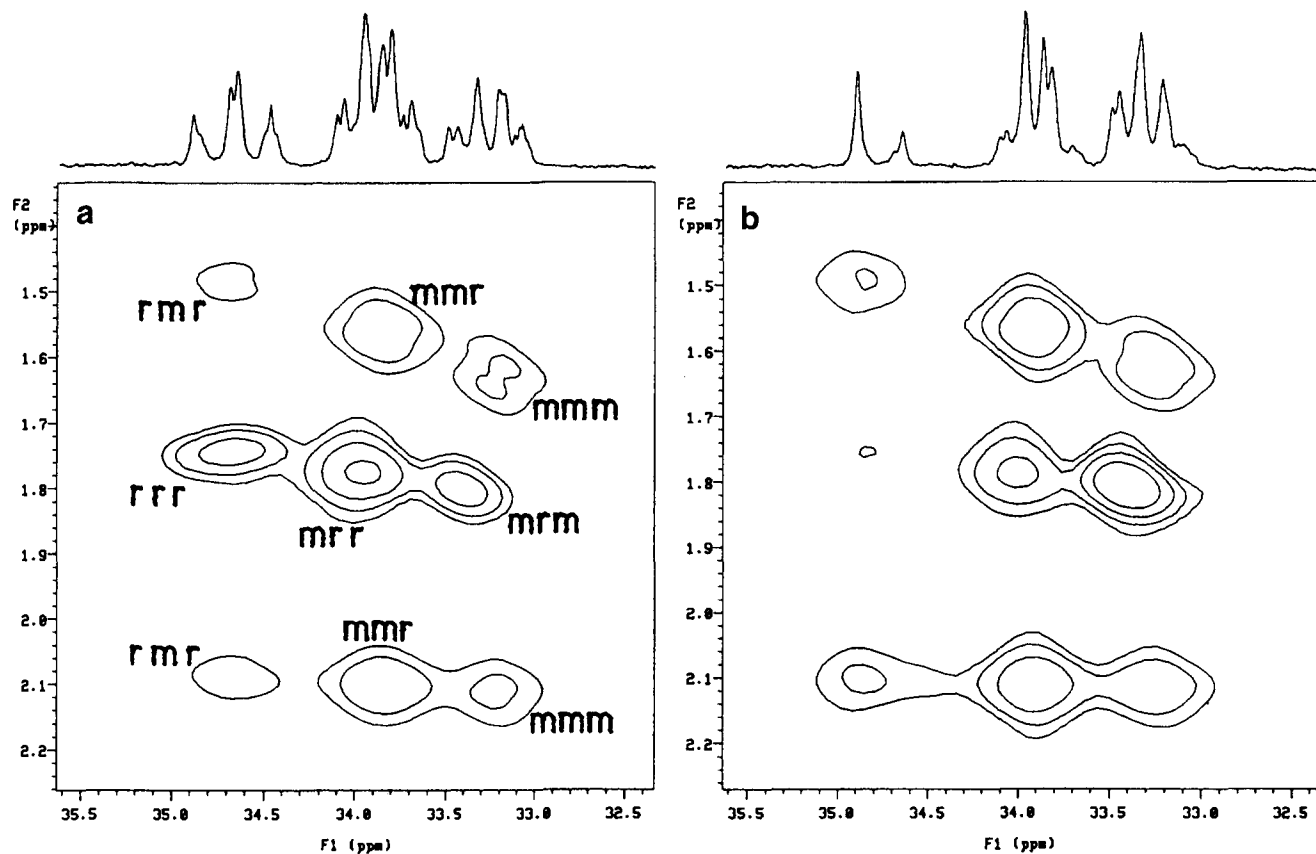| Tetrad	PEA I tetrad content			PEA II tetrad content			Integration limits in ^{13}C n.m.r. (ppm from HMDS)
	Bernoulli ($P_m = 0.53$)	First-order Markov ($P_{r/m} = 0.49$, $P_{m/r} = 0.43$)	Experimental	Bernoulli ($P_m = 0.65$)	First-order Markov ($P_{r/m} = 0.83$, $P_{m/r} = 0.445$)	Experimental	
mmm	0.15 ⎱0.28	0.17₃ ⎱0.28₅	0.27	0.27 ⎱0.42	0.20 ⎱0.44	0.43	32.9–33.6
mrm	0.13 ⎰	0.11₂ ⎰		0.15 ⎰	0.24 ⎰		
mmr	0.26₅ ⎱0.50	0.26₁ ⎱0.49₅	0.51	0.30 ⎱0.46	0.32 ⎱0.42	0.45	33.6–34.3
mrr	0.23₅ ⎰	0.23₄ ⎰		0.16 ⎰	0.10 ⎰		
rmr	0.12 ⎱0.22	0.10 ⎱0.22	0.22	0.08 ⎱0.12	0.13 ⎱0.14	0.12	34.3–35.1
rrr	0.10 ⎰	0.12 ⎰		0.04 ⎰	0.01 ⎰		

Figure 4 Parts of the two-dimensional $^{13}C-^{1}H$ HETCOR n.m.r. spectra of 10% solutions of (a) PEA I and (b) PEA II in C_6D_6, obtained by the inverse HETCOR experiment (HMQC) at 70°C
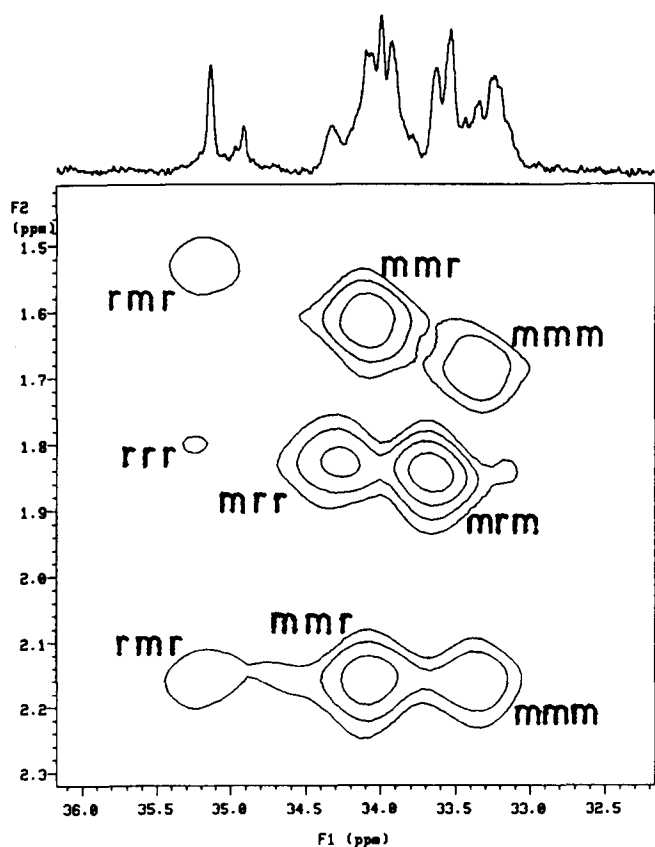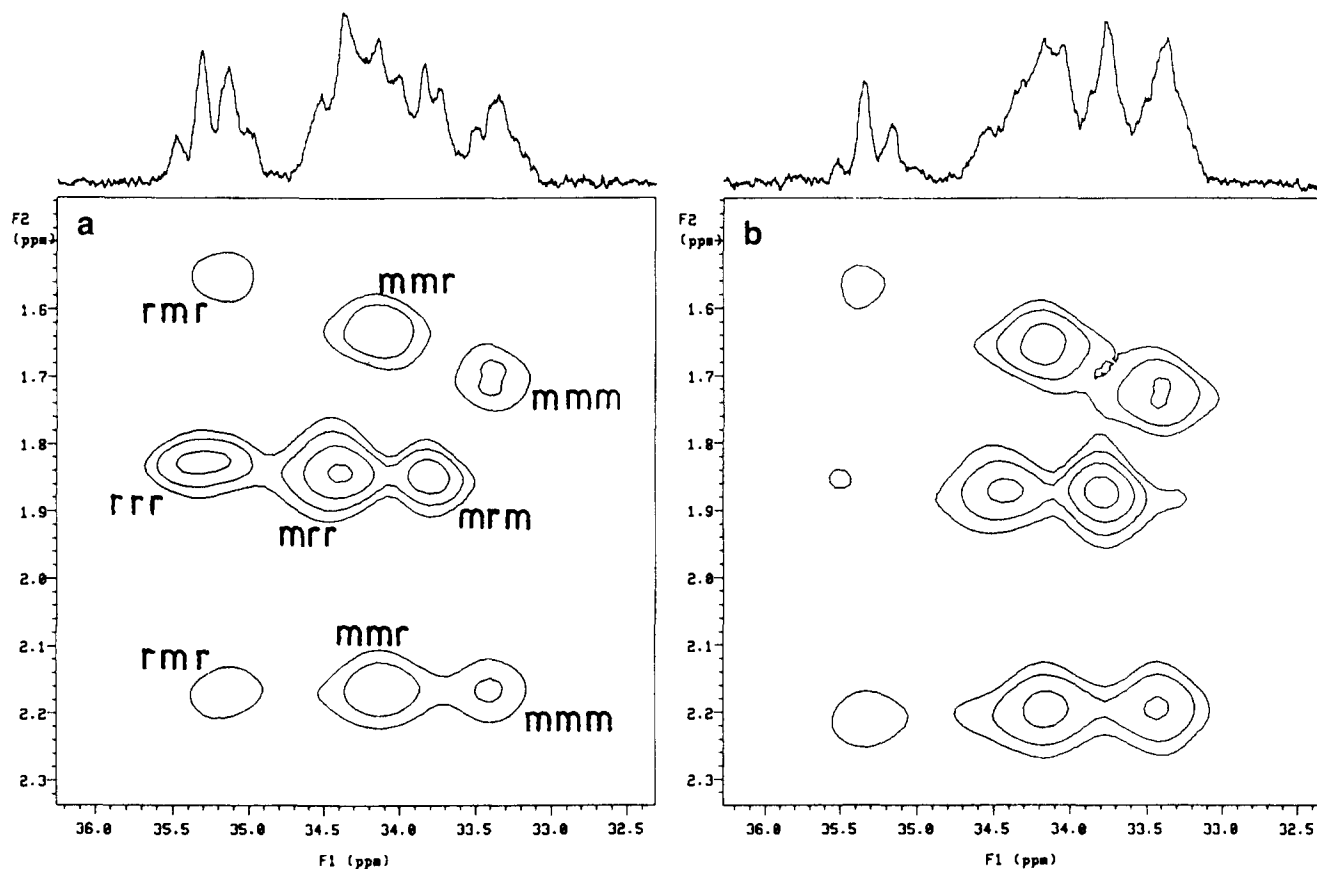

Figure 5 Part of the two-dimensional $^{13}C-^{1}H$ HETCOR n.m.r. spectrum of a 10% solution of PBuA in C_6D_6, obtained by the inverse HETCOR experiment (HMQC) at 70°C

populations from both the Bernoullian and first-order Markov models. For PEHA (*Table 4*) the agreement between experimental and calculated values is somewhat poorer, probably because in the ^{13}C n.m.r. spectra of this polymer (*Figures 2d* and *2e*) the three regions are not clearly separated, and so the integration limits are less well defined. Nevertheless, for all the polymers the results obtained confirm that the tetrad assignments presented in *Table 1* and *Figures 4–6* are correct.

When we look at the $P_{r/m}$ and $P_{m/r}$ values (*Tables 2–4*), we find that only for PEHA II is $P_{r/m} + P_{m/r} \approx 1$ satisfied, as required for Bernoullian statistics. While only slight deviations ($P_{r/m} + P_{m/r} \approx 0.9$) were found for PEA I and PEHA I, which need not be significant[13], for PEA II and PBuA the values found ($P_{r/m} + P_{m/r} = 1.27$ and 1.18, respectively) indicate larger departures from the Bernoullian model with a tendency towards alternating structures. Consequently, we quantitatively analysed in more detail the region of the rrr and rmr tetrads (34.4–35.2 ppm) in the ^{13}C n.m.r. spectra of PEA and PBuA samples. In this region the line intensities are significantly different for PEA I and PEA II (cf. *Figure 2*). Based on the shapes of the HETCOR spectra in *Figure 4*, we assumed that both rrr-centred and rmr-centred hexads would cover the whole region of the rrr and rmr tetrads in the ^{13}C n.m.r. spectrum. This region could be divided into three well separated parts corresponding to pairs of rrr-centred and rmr-centred hexads, assigned by us as shown in *Figure 2*. The experimental intensities were again compared with the calculated hexad populations assuming Bernoullian and first-order Markov

Figure 6 Parts of the two-dimensional $^{13}C-^1H$ HETCOR n.m.r. spectra of 10% solutions of (a) PEHA I and (b) PEHA II in C_6D_6, obtained by the inverse HETCOR experiment (HMQC) at 70°C

Table 3 Experimental and calculated tetrad contents for PBuA obeying Bernoullian or first-order Markov statistics

	PBuA tetrad content				Integration limits in ^{13}C n.m.r. (ppm from HMDS)
Tetrad	Bernoulli ($P_m = 0.65$)	First-order Markov ($P_{r/m} = 0.77$, $P_{m/r} = 0.41_5$)		Experimental	
^{m}mm	0.10	0.12_5	0.12	0.27	0.26	33.0–33.6
mrm	0.11 ⎫	0.09 ⎫		0.15 ⎫		
mmr	0.23 ⎬0.61	0.23 ⎬0.58	0.65	0.30 ⎬0.61	0.66	33.6–34.8
mrr	0.27 ⎭	0.26 ⎭		0.16 ⎭		
rmr	0.13 ⎫0.29	0.10_5 ⎫0.29_5	0.23	0.08 ⎫0.12	0.08	34.8–35.7
rrr	0.16 ⎭	0.19 ⎭		0.04 ⎭		

Table 4 Experimental and calculated tetrad contents for PEHA obeying Bernoullian or first-order Markov statistics

	PEHA I tetrad content			PEHA II tetrad content		Integration limits in ^{13}C n.m.r. (ppm from HMDS)
Tetrad	Bernoulli ($P_m = 0.46$)	First-order Markov ($P_{r/m} = 0.41$, $P_{m/r} = 0.49$)	Experimental	Bernoulli ($P_m = 0.65$)	Experimental	
mmm	0.10	0.12_5	0.12	0.27	0.26	33.0–33.6
mrm	0.11 ⎫	0.09 ⎫		0.15 ⎫		
mmr	0.23 ⎬0.61	0.23 ⎬0.58	0.65	0.30 ⎬0.61	0.66	33.6–34.8
mrr	0.27 ⎭	0.26 ⎭		0.16 ⎭		
rmr	0.13 ⎫0.29	0.10_5 ⎫0.29_5	0.23	0.08 ⎫0.12	0.08	34.8–35.7
rrr	0.16 ⎭	0.19 ⎭		0.04 ⎭		

Table 5 Experimental and calculated hexad contents (rrr-centred and rmr-centred hexads only) for PEA obeying Bernoullian or first-order Markov statistics

	PEA I hexad content			PEA II hexad content		
Hexad	Bernoulli $(P_m=0.53)$	First-order Markov $(P_{r/m}=0.49, P_{m/r}=0.43)$	Experimental	Bernoulli $(P_m=0.65)$	First-order Markov $(P_{r/m}=0.83, P_{m/r}=0.445)$	Experimental
rrrrr	0.02_3 ⎫ 0.04_9	0.03_2 ⎫ 0.05_8	0.06	0.00_5 ⎫ 0.01_5	0.00 ⎫ 0.00_4	0.00_1
rrmrr	0.02_6 ⎭	0.02_6 ⎭		0.01 ⎭	0.00_4 ⎭	
mrrrr	0.05_2 ⎫ 0.11	0.06_1 ⎫ 0.11	0.11	0.02 ⎫ 0.05_6	0.00_3 ⎫ 0.03_9	0.03_7
mrmrr	0.05_8 ⎭	0.04_9 ⎭		0.03_6 ⎭	0.03_6 ⎭	
mrrrm	0.02_9 ⎫ 0.06_2	0.02_9 ⎫ 0.05_3	0.05	0.01_8 ⎫ 0.05_1	0.00_7 ⎫ 0.09_6	0.08_2
mrmrm	0.03_3 ⎭	0.02_4 ⎭		0.03_3 ⎭	0.08_9 ⎭	

statistics (see the Appendix, *Table A1*); for PEA samples these values are summarized in *Table 5*. This table shows that for PEA I both statistical models fit the experimental data reasonably well (the first-order Markov statistics fit better the sums of the hexad pair populations, while the Bernoullian statistics fit better the hexad relations mrrrr/mrmrr). For PEA II (and similarly for PBuA), where mrmrm hexads prevail, the first-order Markov model is unambiguously preferred at the hexad level. From *Table 5* it also follows that no other combination of hexads satisfactorily fits the experimental intensities, confirming the uniqueness of our assignment.

CONCLUSIONS

By means of the inverse ^{13}C–^1H HETCOR (HMQC) n.m.r. spectra we have proved that the assignments of methylene resonances to tetrad structures reported by us recently for PtBuA[7] hold also for other polyacrylates (PEA, PBuA and PEHA). Increasing the size of the side-chain substituent results only in a shift of the main-chain CH and CH_2 resonances (both in the ^1H and ^{13}C n.m.r. spectra) to lower field. The stereochemical structure of PEHA had not been studied before now. For PEA and PBuA, the tetrad assignments of the CH_2 resonances from the ^{13}C n.m.r. spectra, as published recently[4,6], have been revised and partial hexad assignments are possible. From the intensities of the CH_2 signals in the ^{13}C n.m.r. spectra it was established that similarly to PtBuA, PEHA prepared by group transfer or anionic polymerization also obeys Bernoullian statistics. Also, the polymer chains in the PEA sample prepared by group transfer polymerization can be reasonably well approximated by a Bernoullian model. On the other hand, analysis of the CH_2 region at the hexad level confirmed significant departures from Bernoullian statistics (a tendency towards alternating structures) for PEA and PBuA prepared by anionic polymerization; for these polymers, the data can be well described by a first-order Markov model.

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APPENDIX

Irrespective of the statistical model, the following relationships between diads and triads are valid

$$(m) = (mm) + (mr)/2 \tag{A1}$$

$$(mm) + (mr) + (rr) = 1 \tag{A2}$$

While in a polymer chain with a random structure obeying Bernoullian statistics the populations of sequences of any length are determined by the single parameter P_m, for first-order Markov statistics there are two independent probabilities characterizing the addition process, $P_{r/m}$ (the probability that the monomeric unit added to a polymer chain terminated by a racemic diad will generate a *meso* diad) and $P_{m/r}$, and they are given by

the following relations[1]

$$P_{r/m} = \frac{(mr)}{2(rr)+(mr)} \tag{A3}$$

$$P_{m/r} = \frac{(mr)}{2(mm)+(mr)} \tag{A4}$$

When $P_{r/m} + P_{m/r} = 1$, the chain propagation obeys Bernoullian statistics; $P_{r/m} + P_{m/r} < 1$ indicates a tendency towards block formation, while $P_{r/m} + P_{m/r} > 1$ indicates a tendency towards an alternating structure.

The relationships for tetrad populations assuming Bernoullian or first-order Markov statistics in terms of P_m (or $P_{r/m}$ and $P_{m/r}$) are explicitly given elsewhere[1]. Analogous relationships for the populations of rrr-centred and rmr-centred hexads, again assuming Bernoullian or first-order Markov statistics, are given in *Table A1*.

Table A1 Populations of rrr-centred and rmr-centred hexads assuming Bernoullian or first-order Markov statistics

Hexad	Bernoullian model	First-order Markov model
rrrrr	$(1-P_m)^5$	$\dfrac{P_{m/r}(1-P_{r/m})^4}{P_{m/r}+P_{r/m}}$
mrrrr	$2P_m(1-P_m)^4$	$\dfrac{2P_{r/m}P_{m/r}(1-P_{r/m})^3}{P_{m/r}+P_{r/m}}$
mrrrm	$P_m^2(1-P_m)^3$	$\dfrac{P_{r/m}^2 P_{m/r}(1-P_{r/m})^2}{P_{m/r}+P_{r/m}}$
rrmrr	$(1-P_m)^4 P_m$	$\dfrac{P_{m/r}^2 P_{r/m}(1-P_{r/m})^2}{P_{m/r}+P_{r/m}}$
mrmrr	$2P_m^2(1-P_m)^3$	$\dfrac{2P_{r/m}^2 P_{m/r}^2(1-P_{r/m})}{P_{m/r}+P_{r/m}}$
mrmrm	$P_m^3(1-P_m)^2$	$\dfrac{P_{r/m}^3 P_{m/r}^2}{P_{m/r}+P_{r/m}}$